Theory of Surface Excitons in Molecular Crystals

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A theory of surface excitons in molecular crystals is presented using the localized perturbation method. Conditions for the existence of surface excitons and the criterion to determine whether surface exciton states lie above or below bulk exciton states are given in terms of the enviromental shift term and the exciton transfer term within a nearest neighbour approximation. It is shown that localization energies of surface excitons are not sensitive to the crystal thickness. Densities of states for bulk and surface exciton states are calculated. The Davydov splitting of surface excitons is also evaluated.

1. Introduction

The existence of the surface electronic states in crystals has been studied for many years. The role which surface states play in determining the electronic properties of crystals was first discussed by Tamm[1] using a semi-infinite Kronig and Penny model. He showed that the surface states might appear when the surface perturbation is sufficiently strong. When the surface states exist its energy dispersion will be two dimensional separated from the three dimensional dispersion of the bulk state.

Recentry, the possibility of the surface electronic states in molecular crystals has been investigated by taking into account the difference in the interactions of molecules near the surface from those in an infinite crystal. Stern and Green[2] calculated the surface states of anthracene and naphthalene, which might facilitate the injection of electrons and holes into the crystals. The electronic excited surface state, the surface exciton state in crystals plays an important role in optical properties.

Two indepcndent calculations have been performed, which demonstrate the possible conitions for the existence of surface excitons in molecular crystals. Schipper[3] discussed the condition in terms of the resonance integral, so called, exciton transfer term and van der Waals integral, so called, enviromental shift term. He showed that surface excitons exist when the resonance or van der Waals term is greater than the band-width determined by the exciton transfer term.

Hoshen and Kopelman[4] odtained the condition that the absolute valuse of the enviromental shift term must be greater than the exciton transfer term in simple cubic crystals with an inversion center containing one molecule per unit cell. Their calculations are based on the localized perturbation method which was first proposed by Koster and Slater[5]. This method was also by Foo and Wong[6]

for Shockley and Tamm surface state of a semi-infinite linear chain of atoms. In this model the localized perturbation is introduced to form a finite system by the cleavage between two adjacent crystal planes of an infinite (perfect) crystal with the cyclic boundary condition. The exciton transfer terms which couple the two cleaved crystals are set to be zero. The difference between the perfect crystal and the cleaved crystals is treated as the localized perturbation. The surface is then treated as a plane defect of the perfect crystal.

In this paper, we investigate the possible conditions for surface exciton states for molecular crystals with two translationally nonequivalent molecules per unit cell based on the method which was developed by Hoshen and Kopelman[4]. In **2** we shall derive the planewise matrix elements of molecular excitons and introduce the localized perturbation matrix、which causes surface exciton states. Section 3 is devoted to give the energies and the Davydov splitting of surface excitons and the expansion coefficients of the surface exciton wave function. In **4** densities of states for bulk and surface excitons are given. Discussions are given in **5**.

2. Basic Equations and Localized Perturbation Matrix.

The Hamiltonian of a molecular crystal may be written as an usual form:

$$H = \sum_{n\alpha} H^0_{n\alpha} + \sum_{n\alpha\,/\,m\beta} V_{n\alpha,m\beta}\,, \tag{2.1}$$

where $H^0_{n\alpha}$ is the Hamiltonian for a free molecule which is localized at the α-site in the n-th unit cell and $V_{n\alpha,m\beta}$ is the intermolecular pair interaction, which is assumed to be a function of the intermolecular distance.

. Now we consider a perfect crystal with lattice vector $\alpha_1, \alpha_2, \alpha_3$. A set of integer n_1, n_2, l may be used to index the unit cell into which the origin of the unit cell is carried by the translation

$$R_{n,l} = n_1 a_1 + n_2 a_2 + l a_3 \ .$$

Assuming that the perfect crystal is built up from plane crystals (a_1 - a_2 planes) by stacking along the a_3 direction, we define the excited state function localized at the l-th plane as follows.

$$\phi^e_{n\alpha l} = A\,\psi^e_{n\alpha l}\ \mathrm{II}\ \psi^0_{m\beta l}\,, \tag{2.2}$$

where A is the antisymmetrization operator permuting electrons between the molecules and $\psi^e_{n\alpha l}, \psi^0_{m\beta l}$ are the excited and ground state wave function of the free molecule, respectively. In general ψ^0, ψ^e correspond to the bonding and the antibonding orbital states of the free molecules, respectively. The crystal eigenstates are assumed to be constructed by a linear combination of the plane localized excited state function:

$$|\,\mathbf{k}, \alpha, l\rangle = (N_1 N_2)^{-1/2} \sum_n e^{i\mathbf{k}\mathbf{R}_{n,l}}\,|\,n, \alpha, l\rangle \quad , \tag{2.3}$$

where $|\,n, \alpha, l\rangle = \phi^e_{n\alpha l}$ and $\mathbf{k}$ is the dimensional wave vector. When crystals have two translationaly

non-equivalent molecules the exciton wave function is given by

$$\Phi_{k(\pm)} = \frac{1}{2}\left(\mid k, \alpha, l\rangle \pm \mid k, \beta, l\rangle\right) \tag{2.4}$$

The planewise matrix elements between the exciton state and the ground state are given as follows.

$$\begin{aligned}\{H(\mathbf{k})\}_{l,l}^{(\pm)} &= (N_1 N_2)^{-1/2} \sum_{n,m} e^{ikR_n} \left[J(n, 0, l; n+m, 0, l)\right. \\ &+ \left. J(n, \beta, l; n+m, \beta, l)\ (1-\delta_{n,0})\right] \\ &+ \frac{1}{2} \sum_{\substack{n,m \\ r,l'}} \left[D(n, 0, l; m, \gamma, l') + D(n, \beta, l; m, \gamma, l')\right. \\ &\qquad - D(n, \beta, l; m, \beta, l')\,\delta_{l,l'}\ \ \delta_{n,m} \\ &\qquad \left. - D(n, 0, l; m, 0, l')\ \delta_{l,l'}\ \ \delta_{n,m}\right] \\ &\pm (2N_1 N_2)^{-1/2} \sum_{n,m} e^{ikR_n} \left[e^{ik\tau_\beta}\ J(n, 0, l; n+m, \beta, l)\right. \\ &\qquad \left. + e^{-ik\tau_\beta}\ J(n, \beta, l; n+m, 0, l)\right], \end{aligned} \tag{2.5}$$

$$\begin{aligned}\{H(\mathbf{k})\}_{l,l'}^{(\pm)} &= (2N_1 N_2)^{-1/2} \sum_{n,m} e^{ikR_n} \left[J(n, \beta, l; n+m, \beta, l')\right. \\ &\qquad + J(n, 0, l; n+m, 0, l') \\ &\pm e^{ik\tau_\beta}\ J(n, 0, l; n+m, \beta, l') \pm e^{-ik\tau_\beta}\ \left. J(n, \beta, l; n+m, 0, l')\right], \end{aligned} \tag{2.6}$$

where the excitation energy of the free molecule is dropped in eq. (2.5) and $\gamma = 0$, τ_β. The exciton transfer term J and the enviromental shift term D are given as

$$J(n, \alpha, l; m, \beta, l') = \langle A\,\psi^e_{n\alpha l}\,\psi^0_{m\beta l'} \mid V \mid \psi^0_{n\alpha l}\,\psi^0_{m\beta l'}\rangle\ , \tag{2.7}$$

$$\begin{aligned}D(n, \alpha, l; \beta, l') &= \langle A\,\psi^e{}_{n\alpha l}\,\psi^e_{n\alpha l} \mid V \mid A\,\psi^0_{m\beta l'}\,\psi^0_{m\beta l'}\rangle \\ &\quad - \langle A\psi^0_{n\alpha l}\psi^0_{n\alpha l} \mid V \mid A\,\psi^0_{m\beta l'}\,\psi^0_{m\beta l'}\rangle\ . \end{aligned} \tag{2.7}$$

At this point we shall define the surface exciton wave function as follows:

$$\Phi_s^{(\pm)} = \frac{1}{N_3} \sum_l c_l\ (\mathbf{k})\ \Phi_l^{(\pm)}\ , \tag{2.9}$$

where c_l (**k**) are the expansion coefficients for the surface state wave function. With the help of eq. (2.9) crystal eigenstates are given by the following secular equation.

$$\sum_{l'} \mid \langle l \mid H(\mathbf{k}) \mid l'\rangle - E(\mathbf{k})\delta_{l\ l,l'} \mid c_{l'}(\mathbf{k}) = 0\ ,$$

or in matrix form:

$$\mathbf{H}(\mathbf{k})\ \mathbf{c}(\mathbf{k}) = E(\mathbf{k})\,\mathbf{c}(\mathbf{k}) \quad , \tag{2.10}$$

where the diagonal and the off-diagonal elements of the matrix $\mathbf{H}(\mathbf{k})$ are given by eq. (2.5) and eq. (2.6), respectively.

On the other hand, the perfect crystal exciton wave function have the form:

$$\Phi_p^{(\pm)}(K) = \frac{1}{N_3} \sum_l c_l^0(K)\, \Phi_l^{(\pm)}(K) \quad , \tag{2.11}$$

where the matrix elements of $H^0(K)$ are those defined by eq. (2.5) and (2.6) and evaluated for the perfect crystals, *i.e.*, for the bulk excitons. We shall define the perturbation matrix $\Delta(k)$,

$$\Delta(\mathbf{k}) = H(\mathbf{k}) - H^0(\mathbf{k}) \quad . \tag{2.13}$$

The perturbation matrix has finite elements only for planes near the surface and is zero for regions away from the surface. We assume that crystal planes $l = 0,\ N_3 - 1$ are the adjacent planes and the surface crystal planes are obtained by the cleavage between this two planes as is stated in **1**. Under these assumptions planewise matrix elements of $H(\mathbf{k})$ become zero between these planes. The perturbation matrix has the following explicit form:

$$\Delta(\mathbf{k}) = \begin{pmatrix} \{H(\mathbf{k})\}_{N_3-1,\,N_3-1} - \{H^0(\mathbf{k})\}_{N_3-1,\,N_3-1} & -\{N^0(\mathbf{k})\}_{N_3-1,0} \\ -\{H^0(\mathbf{k})\}_{0,N_3-1} & \{H(\mathbf{k})\}_{0,0} - \{H^0(\mathbf{k})\}_{0,0} \end{pmatrix}$$

$$= \begin{pmatrix} -D & -J \\ -J & -D \end{pmatrix} \quad , \tag{2.14}$$

where the enviromental shift term D and the exciton transfer term J within the nearest neighbor approximation are given as follows;

$$D = D(\alpha_3),\quad J = J(\alpha_3) \pm J(\alpha_3 + \tau_\beta)\ cos\varsigma = J_2\ cos\xi,\quad \xi = (k_1 + k_2)\ \tau_\beta, \tag{2.15}$$

Inserting eq. (2.13) to eq. (2.10) we obtain

$$[\Delta(\mathbf{k}) + H^0(\mathbf{k})]\,\mathbf{c}(\mathbf{k}) = E(\mathbf{k})\,\mathbf{c}(\mathbf{k}) \tag{2.16}$$

Equation (2.16) is reduced to the matrix equation which determines $c(\mathbf{k})$ in terms of $c^0(\mathbf{k})$,

$$\mathbf{c} = \mathbf{c}^0\,[E - E^0]^{-1}\,\mathbf{c}^{0-1}\Delta c \ ,$$

or in the explicit form as follows:

$$c_l\ (\mathbf{k}) = \Sigma_{l',l''}\ \frac{c_l^0\ (\mathbf{K})\ c_{l'}^0\ (\mathbf{K})\ \{\Delta\ (\mathbf{k})\}_{l',l''} c_{l''}\ (\mathbf{k})}{\mathrm{E}\ (\mathbf{k}) - E^{\,0}\ (K)}$$

$$= \Sigma_{l',l''}\ D_{l,l'}^0\ (\mathbf{k})\ \{\Delta\ (\mathbf{k})\}_{l',l''} c_{l''}\ (\mathbf{k}) \quad , \tag{2.17}$$

where Green's function G of the perfect (unperturbed) crystal is defined as

$$G_{l,l'}^0\ (\mathbf{k}) = \sum_{k_3} \frac{c_l^0\ (\mathbf{k})\ c_{l'}^0\ (\mathbf{K})}{E\ (\mathbf{k}) - E^0\ (\mathbf{K})} \quad , \tag{2.18}$$

where $k_3 = 2\pi l/N_3$, $l = 0, 1, 2, \ldots, N_3 - 1$.

The matrix equation (2.17) correspond to the usual perturbation expansion for Green's function. The perturbed Green's function is given in matrix form:

$$\mathbf{G} = \mathbf{G^0} + \mathbf{G^0}\ \Delta\ \mathbf{G} = [1 - \Delta G^0\ ]^{-1} G^0 = G^0 + G^0\ [1 - \Delta G^0\ ]^{-1} \Delta G^0 \quad , \tag{2.19}$$

where $\mathbf{G}, \mathbf{G^0}$ are Green's function matrices with elements $G_{l,l'}$, $G_{l,l'}^0$. The poles of eq. (2.19) give the energies of the perturbed system, which are determined by

$$det\ |\ \delta_{l,l'} - R_{l,l'}\ | = 0 \quad , \tag{2.20}$$

where

$$R_{l,l'}\ (\mathbf{k}) = \sum_{l''} G_{l,l''}^0 (\mathbf{k})\ \{\Delta\ (\mathbf{k})\}_{l'',l'} \ .$$

3. Energies and Davydov Splitting of Surface Excitons.

The determinantal eq. (2.20) is reduced to two equations which give the energies of surface excitons:

$$1 + [G_{0,0}^0(E) + G_{0,N_3-1}^0\ (E)]\ \ (D+J) = 0 \quad , \tag{3.1a}$$

$$1 + [G_{0,0}^0\ (E) - G_{0,N_3-1}^0 (E)]\ (D-J) = 0 \quad , \tag{3.1b}$$

where

$$G_{l,l'}^0\ (E) = \frac{1}{N_3} \sum_{k_3} \frac{e^{i(l-l')\ k_3\ a_3}}{E - 2J\cos\ (k_3\ a_3\ )} \quad . \tag{3.2}$$

In eq. (3.2) the energy is measured relative to the diagonal matrix element of the perfect crystal, which is given by

$$E_0 = \{H^0\ (\mathbf{k})\}_{0,0} = 2J\ (a_1\ )\ \cos\xi + 2J\ (a_2\ )\ \cos\eta \pm 2J\ (\tau_\beta)\ \cos\zeta$$

$$+ 2D\ (a_1\ ) + 2D\ (a_3\ ),\ \xi = k_1\ a_1\ ,\ \eta = k_2\ a_2\ ,\ \zeta = (k_1 + k_2\ )\ \tau_\beta \quad .$$

For a finite number N_3, it is difficult to solve eq. (3.1a) and (3.1b) analytically. In the limit $N_3 \to \infty$, one can obtain the solution by replacing the summations by integrations over k_3 in eq. (3.2). From eq. (3.1a) the energy of surface excitons is given by:

$$E_s = -D - \frac{J^2}{D} \quad . \tag{3.5}$$

The following conditions must be satisfied for the existence of surface excitons:

$$(D+J) < 0 \quad or \quad (D-J) > 0 \tag{3.4}$$

At this point we set that the exciton transfer term J is possitive[4,7]. Equation (3.3) is rewritten as

$$E_S^{\pm} = -D - \frac{(J_1 \pm J_2 \cos\xi)^2}{D} \quad , \tag{3.5}$$

which determine the Davydov splitting of surface excitons:

$$E_S^+ - E_S^- = -\frac{4J_1 J_2 \cos\xi}{D} , \tag{3.6}$$

Energies of surface excitons for $N_3 \to \infty$ are shown in Fig.1, where $\cos\xi$ is chosen as 1.

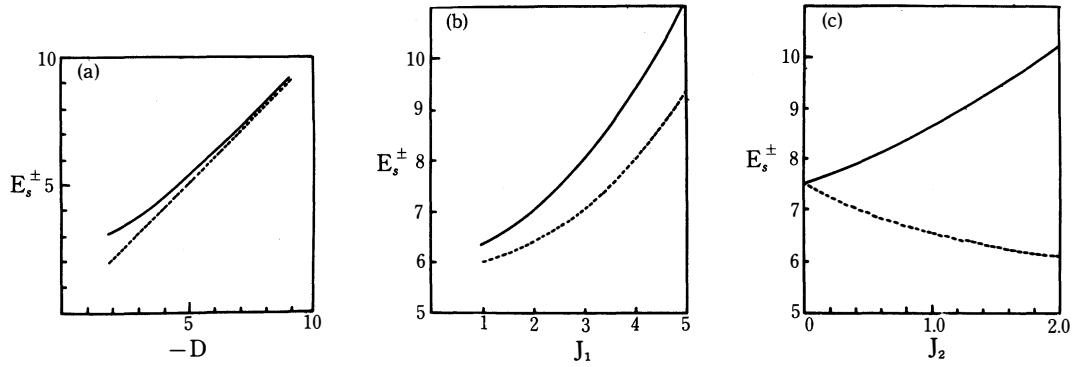

Fig.1 Energies of surface excitons E_s^+ (solid line), E_s^- (dashed line) in the limit $N_3 \to \infty$. The enviromental shift teerm D and the exciton transfer term J_1, J_2 are chosen so as to satisfy the conditions $D+J<0$, $J_1 > J_2$; (a): *vs.* the enviromental shift term. $J_1 = 1.0$, $J_2 = 0.5$ are fixed. (b): *vs.* the ekciton transfer term J_1. $D = -6.0$, $J_2 = 0.5$ are fixed. (c): *vs.* the exciton transfer term J_2. $D = -6.0$, $J_1 = 3.0$ are fixed.

When the energy of surface excitons is obtained the expansion coefficients for the surface exciton wave function are calculated by ep. (2.17).

$$\begin{aligned} c_l(E) &= -[G^0_{l,0}(E)\, D + G^0_{l,N_3-1}(E)\, J]\, c_0(E) \\ &\quad -[G^0_{l,0}(E)\, J + G_{l,N_3-1}(E)\, D]\, c_{N_3-1}(E) \\ &= (-\frac{J}{D})^l \; c_0 \quad , \end{aligned} \tag{3.7}$$

for the symmetric solution $c_0 = c_{N_3-1}$. The localization condition $|J| < |-D|$ which is obtained

from eq. (3.7) coincides with eq. (3.4). The normalized coefficient for the surface plane is given by

$$c_0^2 = \frac{1}{2}[1 - (\frac{J}{D})^2] \quad . \tag{3.8}$$

From eq. (3.1b) the antisymmetric solution corresponding to $c_0 = -c_{N_3-1}$ is also given by eq. (3.3). The symmetric and the antisymmetric solutions are degenerate in the limit $N_3 \to \infty$ when surface exciton states are localized at the plane $l = 0,\ N_3 - 1$.

As is shown in the above calculations, it is easy to give the energy of surface excitons in the limit $N_3 \to \infty$. For a finite N_3, numerical calculations are carried out to give the solution of eq. (3. 1a). The resuts are shown in Fig.2a as a function of N_3, in Fig.2b as a function of D and in Fig. 2c as a function of J_1. Figure la shows thet the surface exciton energies are independent of the crystal plane number and coincide with that for the case of the semi-infinite crystal in the region where N_3 are larger than 10. Hence, the surface cxciton energy can be approximated by the solution for the semi-infinite crystals.

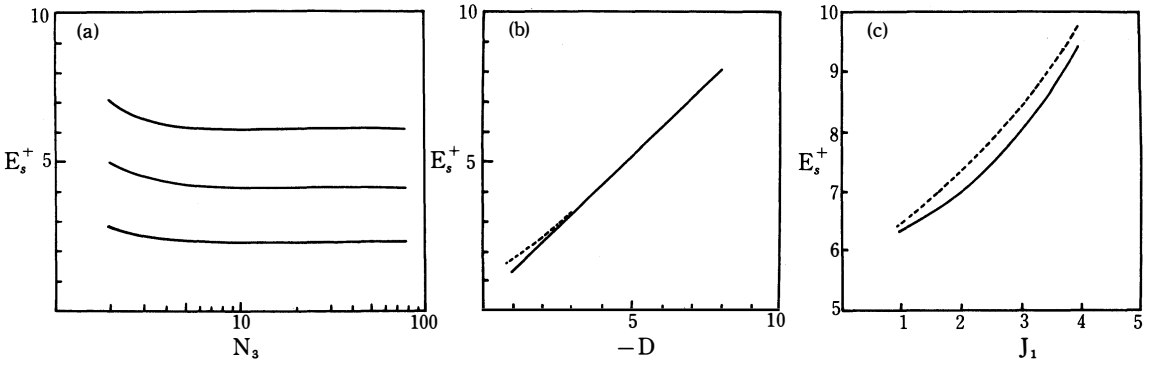

Fig.2 Energies of surface excitons for finite crystal plane number N_3. (a):*vs.* the number of the crystal plane, $J_1 = 0.5$, $J_2 = 0.3$ are fixed. (b):*vs.* the enviromental shift term. Solid line: $N_3 = 10$.Dashed line: $N_3 = 4$, $J_1 = 0.5$, $J_2 = 0.3$ are fixed. (c):*vs.* the exciton transfer term J_1. Solid line:$N_3 = 10$. Dashed line:$N_3 = 4$. $D = -6.0$, $J_2 = 0.5$ are fixed.

4. Density of States for Bulk and Surface Excitons.

The density of states of the perturbed system is given by

$$\rho(E) = \rho_b(E) + \rho_s(E)$$

$$= \frac{1}{2\pi N}\ [Im\,\mathrm{Tr}\,G^0(E) + Im\,\mathrm{Tr}G^0(E)\ \{1 - \Delta G^0(E)\}^{-1}\Delta G^0(E)] \quad , \tag{4.1}$$

where ρ_b, ρ_s are the density of states for bulk and surface exciton states, respectively and Im stands for imaginaly part and Tr for trace. After straightforward calculation, one can obtain the density of states for $N_3 \to \infty$:

$$\rho_b(E) = \frac{1}{\pi N}\, Im\ [G^0_{0,0}(E) + G^0_{0,N_3-1}(E)]$$

$$= \frac{1}{2N_3 J}\left[\frac{(2J+E)}{(2J-E)}\right]^{1/2} \quad ; \; -2J < E < 2J \; , \tag{4.2}$$

$$\rho_s(E) = -\frac{1}{\pi N} Im\left[\frac{\{G^0_{0,0}(E)+G^0_{0,N_s-1}(E)\}^2 (D+J)}{1+\{G^0_{0,0}(E)+G^0_{0,N_s-1}(E)\}(D+J)}\right]$$

$$= \frac{(D+J)^3}{D^2(D-J)}\,\delta(E-E_s) \; ; \; E > 2J \; , \; E < -2J \; , \tag{4.3}$$

where $\dot{E}_s$ are given by eq. (3.3)

From eq. (4.2), the band-width of the bulk exciton is given by the exciton transfer term $4J$. One can easily notice from eq. (4.3) that the surface exciton states are localized outside the bulk exciton band. It is important to give the conditions which determine whether the surface exciton states are localized below or above the bulk exciton state. This conditions are given by the following equations:

$$E_s - 2J = -\frac{(D+J)^2}{D} > 0 \quad , \tag{4.4a}$$

for surface excitons above the bulk one and

$$-2J - E_s = \frac{(D-J)^2}{D} > 0 \quad , \tag{4.4b}$$

for surface excitons below the one.

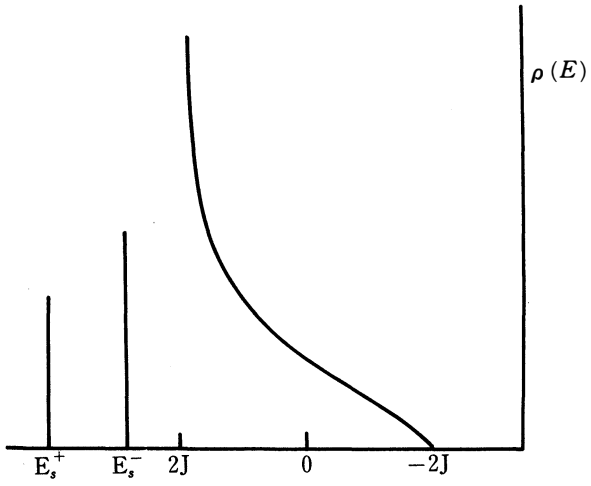

Fig.3

Schematical density of states for bulk and surface exciton states. In this figure, surface exciton states are localized above bulk exciton states for negative values of the enviromental shift term. As is shown in fig.5, the intensity of E_s^- is larger than that of E_s^+.

From eqs. (4.4), the surface exciton states are localized above the bulk exciton state for the condition $D<0$ and below the one for the condition $D>0$. The densities of states for bulk and surface excitons are shown schematically in Fig.3. As is shown in Fig.3, two splitting lines are the Davydov splitting of surface excitons. Equation (4.3) is rewrtten as

$$\rho_s^{\pm}(E) = I_s^{\pm}\,\delta(E-E_s^{\pm}) \quad , \tag{4.5}$$

where the intensities of the δ-function are given by

$$I_s^{\pm} = \frac{(D+J_1 \pm J_2 \cos\xi)^3}{(D-J_1 \pm J_2 \cos\xi)\, D^2} \quad , \tag{4.6}$$

and the intensity ratio of the Davydov components is given by

$$I_s^{+}/I_s^{-} = \frac{(D+J_1 \pm J_2 \cos\xi)^3 \ (D-J_1+J_2 \cos\xi)}{(D+J_1-J_2 \cos\xi)^3 \ (D-J_1-J_2 \cos\xi)} \quad , \tag{4.7}$$

The intensities I_s^{+} and I_s^{-} are shown in Fig.4. It is clear from Figs.4 that the intensity ratio given by eq. (4.7) is smaller than unity for all values of D, J_1, J_2. This result is shown in Fig.3. The behaviors of the intensities I_s^{+}, I_s^{-} as a function of D, J_1, J_2 qualitatively agree with that of the expansion coefficients given by eq. (3.7) which determines the degree of the localization of surface excitons. The result that the localization of the surface exciton state increases with an increase in the magnitude of D is already obtained by Hoshen and Kopelman[4]. The decrease of the localization with an increase of J is explained by the fact that the surface exciton easily penetrates into the bulk state with an increase of the exciton transfer term J along a_3 direction.

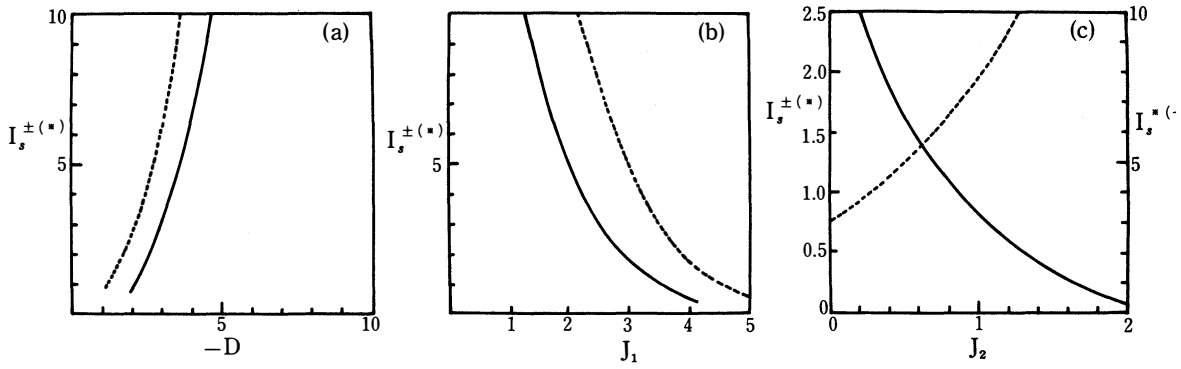

Fig.4 Intensities of the density of states for surface excitons $I_s^{*+} = N_3 I_s^{+}$ (solid line), $I_s^{*-} = N_3 I_s^{-}$ (dashed line). (a): *vs.* the enviromental shift term. $J_1 = 0.5$ $J_2 = 0.3$ are fixed. (b): *vs.* the exciton transfer term J_1. $D = -6.0$, $J_2 = 0.5$ are fixed. (c): *vs.* the exciton transfer term J_2. $D = -6.0$, $J_1 = 3.0$ are fixed.

5. Discussions.

As we have seen in preceding sections, the conditions for the existence of surface excitons in molecular crystals are given in terms of the enviromental sfift term D and the exciton transfer term J. The results are summarized as follows:

Case (1) Surface exciton states are localized above the bulk exciton state under the conditions;

$$(D+J) < 0 \quad and \quad D < 0 \quad ;i.\ e., \quad D+J_1 \pm J_2 \cos\xi < 0 \quad .$$

Case (2) surface exciton states are below the bulk state under the conditions;

$$(D-J) > 0 \quad and \quad D > 0 \quad ;i.e., \quad D-J_1 \pm J_2 \cos\xi > 0 \quad .$$

In aromatic hydrocarbon crystals, the enviromental shift term D is negative and its absolute value is larger than that of the exciton transfer term J. The conditions for Case (1) seem to be satisfied in these crystals.

Recently Turlet and Philpott[8,9] have measured the reflection spectra of crystalline anthracene and tetracene, over a range of temperatures from 180 to 1.6 K.Two anomalous reflectivity minima located above the zero phonon line of bulk excitons are observed and they become more sharpe with the decrease of temperature. These features are common to anthracene and tetracene. Turlet and Philpott tentatively attributed two minima to surface excitons. For tetracene crystal, the enviromental shift term of bulk excitons is about -2000 cm^{-1}, implying that all the planewise enviromental shift terms are negative and its absolute values are larger than the cxciton transfer term. According to their experimental results, two reflectivity minima are observed approximately 5 cm^{-1} and 160 cm^{-1} above the b-polarized bulk exciton transition at 18694 cm^{-1} for tetracene crystal and are 7 cm^{-1} and 195 cm^{-1}above the one at 25108 cm^{-1} for anthracene crystal.

Brodin *et al.*[10] reported a similar reflectivity minima, and Glockner and Wolf[11] observed two emission lines at 25298 cm^{-1} (I) and 25103 cm^{-1}(II) above the fluorescence at 25097 cm^{-1} for anthracene. Several assignments are given for the line (II). Brodin *et al.* assigned line (I) to emission from the surface exciton and line (II) to fluorescence due to the zero phonon line of the bulk exciton. An alternative explanation is given by Turlet and Philpott[8] that line (II) is the emission from a second surface state to the first surface state. Assignment of both lines, (which are observed as dips in the reflection spectra) to surface excitons seems to rationalize their similar behaviors with respect to temperature.

As we have shown in preceding sections, the Davydov splitting of surface excitons is expected for crystals with two translationally non-equivalent molecules per unit cell such as anthracene and tetracene. The origin of the two reflectivity minima may be attributed to the Davydov splitting of surface excitons. In this cace, the energy of the Davydov splitting is given by eq.(3.6). Using the energies anb the Davydov splitting of bulk and surface excitons, one can calculate the enviromental shift term and the exciton transfer term. At this stage, we can not determine the absolute values of D, J_1, J_2 owing to a lack of experimental data. The Davydov splitting of surface excitons becomes more clear by the observation of the a- and b-polarized reflection spectra of the (001) face of these molecular crystals.

As a final remark, we mention to Case (2). The rare gas solid have the positive enviromental shift term. The condition for Case (2) seems to be satisfied in these crystals. Anomalies in the reflection spectra have been observed below the bulk exciton band in these crystals[12]. These experimental results qualitatively agree with our theoretical ones.

The investigation of the effect of surface excitons on the reflection spectra will be shown in the following paper[13].

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